

COATINGS. ENAMELS

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PRODUCTION OF SILICATE COATINGS FROM GLASS-FORMING COLLOIDAL SOLUTIONS

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Compositions and principles of preparation of glass-forming colloidal solutions resistant to gel formation and based on tetraethoxysilane are given. The processes occurring in heating the products of thermal deposition of the solutions are considered. Using a mathematical experiment design, the effect of molybdenum, manganese, and copper oxides on the strength of adhesion of the coating to the substrate is determined. The molding conditions and the properties of protective vitreous coatings are indicated.

The development of space technology, electronics, and robotics generates a demand for new construction materials with a number of specific service qualities. Glass and glass-based materials are of special interest in this context. The reasons preventing wider application of glass in working parts of instruments include low mechanical strength and, in the case of polyfunctional glass coatings, also high temperatures of silicate-glass fusion. Production of new special types of glass using traditional technology requires substantial energy consumption. Therefore, the use of sol-gel technology in glass production and upgrading of this technology acquire special importance.

The sol-gel method and variations of it are now widely used in making certain solid glass articles and especially in the production of glass coatings on glass, metal, ceramic, and plastic substrates [1 – 3].

A variant of the sol-gel method is solution technology, which is based on using true and colloidal solutions [4]. Employing precision heat treatment of these solutions, it is possible to produce solid products [5], and by means of rapid heating one can obtain a batch mixture and subsequently a thin vitreous film [4].

Solution technology is preferable in developing vitreous coatings in silicate systems whose formation is not restricted by the low thermal stability of the substrate material.

The present paper considers the production of glass-forming solutions resistant to gel formation and coagulation and based on tetraethoxysilane (TEOS) and the development of technological principles of using these solutions in the synthesis of polyfunctional glass coatings for steel.

In this context, the study of all stages of production of the indicated solutions (distillation and hydrolysis of TEOS, mixing the hydrolyzate with certain components) is of undeniable interest. It is important to study thoroughly the processes occurring in glass-forming solutions in the course of deposition and fusion of their components.

The initial glass compositions for synthesis of coatings from glass-forming solutions satisfy the general formula

$$(70-x)\text{SiO}_2 - x\text{RO} - 30\text{Li}_2\text{O},$$

where $x = 5, 10, 15$; $R = \text{Ca, Ba}$.

The given system has a wide range of glass formation [6]; however, without modifying the initial ternary system, it is impossible to combine the advantages of its high thermo-mechanical parameters and chemical stability with adhesion to the steel substrate.

Silicon-bearing glass-forming solutions are based on the colloidal component $(\text{SiO}_2 \cdot n\text{H}_2\text{O})$. In practice, a colloidal solution of silicic acid is produced predominantly from orthosilicic acid ethers [7].

The process of TEOS hydrolysis depends largely on its structure and properties, which vary in time [8]. Monitoring of the state of TEOS was implemented by measuring the refractive index on an IRF-22 refractometer. It is found that the refractive index varies in the course of storage of TEOS. The present experiment used TEOS of grade MRTU-6-09-3074-66 freshly distilled at a temperature of 167°C.

Stable silicic acid sol (hydrolyzate) was produced by the TEOS hydrolysis reaction. The molar proportion $\text{Si}(\text{OC}_2\text{H}_5)_4 : \text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O}$ was $1 : (1.5...2) : 4$. The stabilizer of the water-alcohol solution of TEOS and the catalyst

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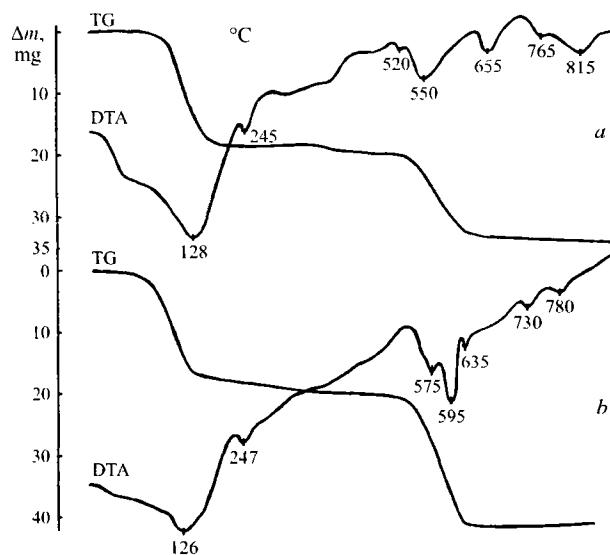


Fig. 1. Differential thermal analysis curves of the products of thermal deposition of GCS of the systems $\text{LiNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ (a) and $\text{LiNO}_3 - \text{Ba}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ (b).

of the hydrolysis reaction were 0.03 – 0.05 mole of HCl . This quantity of hydrochloric acid is necessary to reach a pH equal to 2, which corresponds to the isopotential point for aqueous solutions of colloidal SiO_2 [5].

However, as noted by the authors in [7], freshly distilled hydrolyzate is not a source of SiO_2 for glass-forming solutions, and traces of silicic acid are absent from it. This is supported by the complete absence of SiO_2 precipitate when fresh hydrolyzate is deposited by pulverization on a metal substrate (steel Kh18N10T) heated to 550°C. Therefore, the hydrolyzate requires a certain time for maturing.

The hydrolysis process was monitored by measuring the refractive index. This value in fresh hydrolyzate is 1.383. The refractive index of the hydrolyzate is stabilized on the fifth day (1.378). Consequently, glass-forming solutions were prepared from the hydrolyzate after aging for 5 – 28 days. Longer storage makes the hydrolyzate unsuitable due to its high viscosity.

Solutions corresponding to the specified glass compositions were prepared from the hydrolyzate and nitrates of alkali and alkali-earth metals. To eliminate weighing errors caused by the high hygroscopicity of the majority of these salts, it was proposed that standard nitrate solutions produced by the reaction of the corresponding metal carbonates with nitric acid be used.

The preparation of the glass-forming solutions was carried out in conformity with the recommendations given in [4]. The duration of gel formation of the developed solutions ($\text{pH} = 1.5 - 2.5$) was 38 – 41 days.

Since the main component of these solutions is colloidal silica, the term used in this study was “glass-forming colloidal solutions” (GCS).

To produce a glass coating of thickness providing high service parameters (chemical resistance, microhardness, etc.), GCS should be deposited on a heated substrate surface, whose temperature depends largely on the type of material. In certain cases [2], an ultrathin (0.1 – 1.0 μm) insulating glass coating is needed. Such a thickness is achieved by immersing the substrate material in the GCS or gel, possibly with protracted holding (sometimes up to 48 h), slow drying, and heat treatment. The immersion and drying stages in this case are difficult to shorten, because of the risk of cracking and scaling of the coating [1]. Pulverization deposition of GCS on a heated substrate (thermal deposition) makes it possible to obtain glass coatings 10 – 20 μm thick (in a single spray-coating cycle). It should be noted that the coating formation temperature increases in this case, and for the compositions considered it is within the range of 800 – 870°C.

It was established that for the developed GCS the steel substrate should be heated to 300 – 600°C before spraying. At lower temperatures the substrate is cooled rapidly, and the GCS flows off. Heating of the steel above 600°C leads to substantial losses of solution, and the thermal-deposition products form a coarsely disperse layer nonuniformly distributed over the surface, which precludes obtaining a continuous glass coating.

Using DTA (a Paulik – Paulik – Erday system derivatograph) the processes occurring in products thermally deposited at 550°C and corresponding to the glasses $60\text{SiO}_2 - 10\text{CaO} - 30\text{Li}_2\text{O}$ and $60\text{SiO}_2 - 10\text{BaO} - 30\text{Li}_2\text{O}$ were studied (Fig. 1). The endothermic effects at temperatures of 126 and 128°C on both diffraction patterns and the mass loss of 22 – 25% in the samples are caused by removal of residual physically bound water. The similar values of the temperature of dehydration of the thermal-deposition products (material mixtures) may indicate equal degrees of dispersion. The endothermic effects at a temperature of 245 – 247°C are related to melting of lithium nitrate [9]. Subsequent mass losses in the samples are not accompanied by significant changes in the DTA curve.

It should be noted that the material mixtures lose 25% of their mass within the temperature interval of 20 – 540°C. The endothermic effects in the mixture of $\text{LiNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ at temperatures of 520 and 550°C and in the mixture of $\text{LiNO}_3 - \text{Ba}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ at temperatures of 575 and 595°C are caused by decomposition of calcium and barium nitrates. In this period, the sample mass decreases sharply (by 24 – 26%), and altogether the material mixture loses around 50% of its mass. Several endothermic effects in the mixture of $\text{LiNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ in the temperature interval of 655 – 815°C and in the mixture of $\text{LiNO}_3 - \text{Ba}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ at temperatures of 635 – 780°C correspond to the appearance of eutectics of binary and ternary compounds of SiO_2 , CaO , Li_2O , and BaO .

Accordingly, the silicate formation temperature in these material mixtures is 100 – 120°C lower than in traditional



Fig. 2. Products of thermal deposition of GCS ($\times 790$).

mixtures prepared from silica and metal carbonates. However, within the temperature range of $200 - 540^\circ\text{C}$, no significant mass changes or reactions between the components occur in the material mixtures. Consequently, it can be assumed that as the GCS is thermally deposited on the heated substrate, the only possibility is recrystallization of nitrates [10], resulting in the appearance of more defective and smaller crystals. It is obvious that the limiting stage in silicate formation in these mixtures is decomposition of the GCS components to metal oxides. The investigated material mixtures exhibited a somewhat lower temperature of decomposition of calcium, lithium, and barium nitrates than the reference data in the literature [9].

Microscope studies (a NEOPHOT-21 microscope) showed that the thermal-deposition products of the GCS of the composition $\text{LiNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{SiO}_2 \cdot n\text{H}_2\text{O}$ deposited by pulverization on a quartz plate at 550°C have the form of clear regular hemispheres with significant size dispersion. The particle diameter varies from 10 to $40 \mu\text{m}$ (Fig. 2).

The phase composition of the products resulting from deposition of the GCS on the quartz plate surface was identified using x-ray phase analysis (DRON-3). The layer produced in this way represented a compact disperse gray-white powder. No crystalline phases were detected in the powders of the $\text{Li}_2\text{O} - \text{CaO} - \text{SiO}_2$ system, whereas $\text{Ba}(\text{NO}_3)_2$, which decomposes at a higher temperature (592°C) than the other nitrates, was recorded in the $\text{Li}_2\text{O} - \text{BaO} - \text{SiO}_2$ system. It should be noted that no crystalline modifications of SiO_2 were detected. Thus, the material mixtures produced by thermal deposition of GCS in the temperature range of $500 - 600^\circ\text{C}$ consist of finely disperse x-ray-amorphous calcium, lithium, and silicon oxides and partly dehydrated barium nitrate.

Based on the DTA and the x-ray phase analysis and calculated TCLE values according to Appen ($110 \times 10^{-7} - 130 \times 10^{-7} \text{ K}^{-1}$), the composition $60\text{SiO}_2 - 10\text{CaO} -$

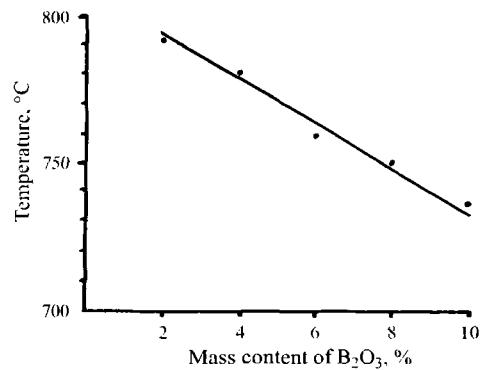


Fig. 3. Effect of B_2O_3 content on the temperature of formation of the vitreous phase in the coating.

$30\text{Li}_2\text{O}$ was selected for production of polyfunctional glass coatings with anticorrosion properties.

A decrease in the formation temperature and improvement of the adhesion of the glass coating to the steel substrate were achieved by improving the mixture composition. Taking into consideration the recommendations given in [11], in order to improve the thermomechanical and covering properties of the glass coating and decrease the surface tension, B_2O_3 was introduced into the initial ternary composition in an amount of 2, 4, 6, 8, and 10% above 100% by means of a concentrated boric acid solution. The results of a polythermal analysis of glass coatings with varying B_2O_3 content indicate its positive effect on lowering the temperature of vitreous-phase formation and the glass surface tension (Fig. 3). The highest fusibility is shown by the composition with 10% B_2O_3 . At the same time, due to the low solubility of H_3BO_3 , it is impossible to obtain a GCS with the required total weight content of the components exceeding 5%. Therefore, the glass-coating composition with 6% B_2O_3 was selected for subsequent experiments.

Combined use of CuO , MnO , and MoO_3 was suggested for improving the adhesion properties of the glass coating. These oxides have an integrated effect; along with improvement of adhesion, they decrease the surface tension (MoO_3) and the viscosity (MnO) and increase the electrical conductivity and the corroding capacity (CuO). These components were added to the GCS in the form of solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The effect of the activator content on the adhesive strength was determined using mathematical design of the experiment. The variables were the concentrations of $\text{MoO}_3 X_1$, $\text{MnO} X_2$, and $\text{CuO} X_3$. The response function Y was taken to be the surface area (%) of the glass coating that remained on the steel after testing the adhesive strength (GOST 24-788-81). The variation interval for the independent variables was selected based on published data [11].

Computer calculations gave regression equations relating the adhesive strength to the concentration of MoO_3 , MnO ,

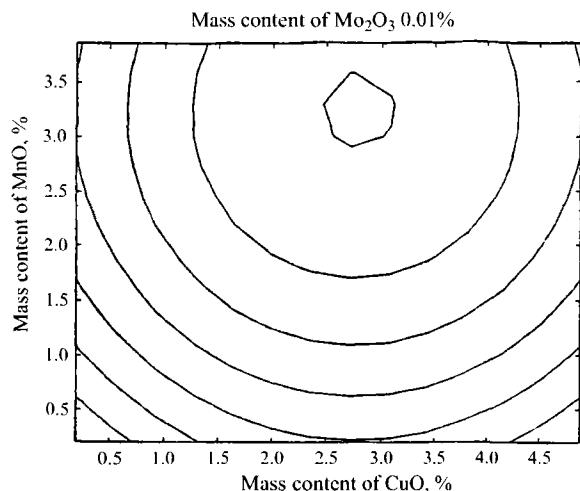


Fig. 4. Response surface.

and CuO in the glass-coating composition and the response surface (Fig. 4)

$$Y = (22.52 \pm 0.4) + (0.98 \pm 0.01)X_1 + (3.03 \pm 0.17)X_2 + (2.62 \pm 0.16)X_3 - (0.49 \pm 0.08)X_1^2 - (0.47 \pm 0.06)X_3^2.$$

An additional regression equation was obtained using an orthogonal matrix:

$$Y = (30.27 \pm 0.4) + (0.98 \pm 0.01)X_1 + (2.49 \pm 0.11)X_2 + (2.92 \pm 0.17)X_3 - (2.15 \pm 0.17)X_1^2 - (3.19 \pm 0.17)X_3^2.$$

Owing to that, the effect of the parameters (X_1 , X_2 , X_3) on the response function was determined within the limits of one step. An analysis of the equations (the method of approximated calculation of the significance coefficients) and the response surfaces shows that the increase in the adhesion is proportional to the MoO_3 concentration; however, the effect of this factor on the level of adhesion is slight. A decisive effect on the adhesion increase is exerted by simultaneous introduction of MnO and CuO . The function has an extremum corresponding to a content of 3.2% MnO and 2.8% CuO .

As a result of the investigations, a method for carrying out TEOS hydrolysis and monitoring the process has been developed, which makes it possible to obtain stable glass-forming colloidal solutions based on $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and metal nitrates with high reproducibility of the compositions. An analysis of the stages of thermal deposition and melting of GCS indicates that the decrease in the glass-formation temperatures in GCS mixtures by 100–120°C compared to

standard mixtures is primarily due to their activation in the course of deposition and a decreased size of the reacting-component particles.

In searching for the optimum composition for a polyfunctional GCS glass coating on steel substrates, the authors took into consideration the solubility of the salts (the GCS components), the duration of transformation of the GCS into a gel, and the data of a polythermal analysis, a DTA, an x-ray phase analysis, and mathematical design of an experiment.

The glass coating obtained by modifying the model glass has the following composition: $60\text{SiO}_2 - 10\text{CaO} - 30\text{Li}_2\text{O} - 6\text{B}_2\text{O}_3 - 3.2\text{MnO} - 2.8\text{CuO}$. This coating has high thermo-mechanical parameters: thermal resistance 350–400°C (GOST 25535–82), microhardness 5000–5400 MPa (PMT-3 instrument), adhesion 4–5 points (GOST 24-788-81), corrosion resistance 0.17–0.20 mg/cm² (GOST 24788-81) (was determined by the weight loss after boiling in 4% acetic acid for 1 h). The temperature of glass-coating formation is 850°C.

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